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REPORT

MRL-R-775

THE EFFECT OF CRYSTAL ORIENTATION ON GROWTH

ON POLYCRYSTALLINE TNT

William S. Wilson

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ABSTRACT

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expansion on thermal cycling is large in a particular direction if
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intercrystalline stresses. Growth is smaller when the crystals are
so arranged that there are no such interactions and the inter-
crystalline stresses generated in that direction are small. Creamed
TNT with its random crystal orientation generates equal intercrystal-
line stresses in all directions on thermal cycling, and growth is
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16. ABSTRACT (If this is security classified, the announcement of this report will be similarly classified):

Dimensional instability of polycrystalline TNT depends markedly on crystal orientation within the specimen. Growth or irreversible expansion on thermal cycling is large in a particular direction if there is a "texture" of crystals with high and low coefficients of thermal expansion in that direction which interact to produce large intercrystalline stresses. Growth is smaller when the crystals are so arranged that there are no such interactions and the intercrystalline stresses generated in that direction are small. Creamed TNT with its random crystal orientation generates equal intercrystalline stresses in all directions on thermal cycling, and growth is consequently equal in all directions. These results are consistent with the "ratchet" mechanism proposed previously to account for growth in polycrystalline TNT.

C O N T E N T S

*   *   *

THE EFFECT OF CRYSTAL ORIENTATION ON GROWTH

OF POLYCRYSTALLINE TNT

1. INTRODUCTION

Dimensional instability (also described as growth or irreversible expansion) of TNT-based explosives on thermal cycling can have important effects on tight-fitting munitions fillings, particularly those in thin casings and which contribute to structural integrity, and has been the subject of investigation both here and overseas. Experiments at establishments overseas have shown that growth of RDX/TNT compositions depends on both the number of thermal cycles to which the charge is subjected and the maximum temperature experienced, and have linked the growth phenomenon with the well-documented anisotropic thermal expansion of TNT without proposing any entirely satisfactory mechanism to account for its occurrence [1,2]. Investigations carried out at Materials Research Laboratories have confirmed that growth of creamed commercial TNT (an array of small randomly oriented TNT grains) similarly increases with the number of thermal cycles, and also increases linearly with the upper temperature of the cycle in such a manner as to suggest that a critical temperature of about 37°C must be exceeded during the cycling process for any growth to be observed [3]. (This suggestion has subsequently been confirmed by cycling creamed commercial TNT below this temperature, under which conditions no growth could be detected [4]). It was shown that growth also depends critically on the presence in the TNT of such impurities as the isomeric trinitrotoluenes and dinitrotoluenes which can form low melting eutectic mixtures with the major constituent, 2,4,6-trinitrotoluene. Furthermore it was found that growth in creamed TNT is accompanied by a change in the surface texture of the charge from a smooth, marble-like machined finish to a more crystalline appearance. This surface change has been described as "roughening" or "wrinkling" in non-cubic metal systems which also exhibit anisotropic thermal expansion [5,6], and in TNT charges appears to be attended by a degree of recrystallisation.

These observations prompted us to propose a sequence of events to account for irreversible expansion of polycrystalline TNT on thermal cycling, based on the "ratchet" mechanism demonstrated by Burke and Turkalo for a

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zinc bicrystal system [7]. Briefly, it was proposed that anisotropic
thermal expansion of TNT generates shearing stresses at the grain boundaries.
These shearing stresses increase with temperature until the elastic limit
is reached, whereupon greater stresses are relieved by intracrystalline slip
or twinning. Above a critical temperature, the melting point of a eutectic
mixture of TNT and its major impurities, some mass transfer process becomes
possible (probably grain boundary sliding or a form of dynamic recrystal-
lisation), which relieves these intercrystalline stresses. On cooling, the
anisotropic contraction generates shearing stresses at the grain boundaries
in the reverse direction, which are also relieved by the mass transfer
process. Below the eutectic melting temperature these transfer processes
are no longer possible, and the grain boundaries are able to support the
stresses again. These stresses increase with decreasing temperature until
the elastic limit is reached, whereupon additional stresses are once more
accommodated by intracrystalline slip and twinning. As the temperature
rises again in the next cycle the stresses decrease to zero and are then
regenerated in the reverse direction, and the sequence of events is repeated.

Shearing stresses generated at grain boundaries as a consequence of
anisotropic thermal expansion must depend critically on the orientation of
the grains both to their common boundary and one to another. If these
shearing stresses constitute the driving force responsible for growth of
polycrystalline materials, then this fact should be reflected in a dependance
of growth on grain orientation within the crystalline matrix. This paper
describes results of some experiments designed to consider the influence of
crystal orientation on the irreversible thermal expansion of polycrystalline
TNT.

2. EXPERIMENTAL AND RESULTS

The crystal orientation within cylindrical TNT castings has been
described by Williamson [8], and is illustrated in Figure 1. Briefly,
crystallisation of clear cast TNT commences from the outside surface of the
cylinder at a "chilled layer" or "cooling selvage" composed of spherulites
[9]. From this chilled layer long crystals of TNT grow radially inwards
from the wall of the cylinder until they meet at the axis; mutual inter-
ference is occasionally insufficient to check further growth, and some
crystals project for short distances beyond the axis. Elongated crystals
also grow perpendicular to the flat base of the cylinder, approximately
parallel to the axis, and meet crystals growing radially from the wall of
the cylinder on the curved surface of a cone. Creamed TNT, or "TNT poured
cloudy", is prepared from a slurry of small crystals in molten TNT. Again
a chilled layer or cooling selvage is formed at the outside of the casting,
but the interior consists of a random array of small crystals as shown in
Figure 1.

For the current investigation a series of cylinders was prepared from
the same batch of commercial TNT but with a variety of crystal orientations
as shown in Figure 2. First, four creamed TNT charges were cast in finger-
moulds 150 mm long and 20 mm in diameter preheated to 60°C. Cylinders
50.8 mm long and 12.7 mm diameter (2.00 inches by 0.50 inches diameter)
were machined from these castings using a lathe, removing the chilled layer

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on both the curved surface and the base of the cylinders. By this means samples with *random* crystal orientation were obtained. Second, four clear-cast TNT charges were prepared in the preheated finger-moulds and machined into cylinders of the same dimensions (50.8 mm long and 12.7 mm diameter (2.00 inches by 0.50 inches diameter)). Again the chilled layer was removed during machining, and the conical region at the base of the casting in which the crystals were aligned parallel to the axis of the cylinder was avoided.' Thus specimens with a *radial* orientation of crystals were obtained. Third, a 200 mm clear-cast TNT charge was prepared in a pre-heated mould, and four cylinders of the same dimensions were machined from the conical region in which the TNT crystals were aligned parallel to the axis of the charge. As it happens the crystal alignment was not perfectly parallel throughout, and the specimens obtained were described as possessing a *"pseudo-axial"* orientation, with a collar of apparently random crystal orientation midway along the specimen. A single specimen was obtained, however, in which the orientation was much closer to an *axial* alignment. For the sake of convenience the samples with random, radial, "pseudo-axial" and axial alignments were designated specimens 1, 2, 3 and 4.

Despite the fact that they were all prepared from the same batch of TNT, samples from specimens 1, 2 and 3 (random, radial and "pseudo-axial" TNT) were analysed for impurity levels using gas chromatography. Material from specimen 4, with the more perfect axial alignment, was machined from the same casting as specimen 3. The results of these analyses are given in Table 1 below. It was rather surprising to find that the analysis figures varied from one specimen to another. The "pseudo-axial" specimen 3 had the lowest impurity content, followed by the radial sample 2, the highest impurity content being in the creamed TNT (random orientation, sample 1). This pattern follows decreasing grain size in the specimen, visible in Figure 2, and these observations appear to be consistent with our belief that impurities in polycrystalline TNT tend to concentrate at the grain boundaries rather than being dispersed evenly through the polycrystalline matrix. Thus as grain size increases the proportion of grain boundaries decreases and the excess impurities may be swept along ahead of the growing crystal front.

TNT cylinders of the various crystal orientations were cycled - 4 to 47°C, 0 to 54°C and 10 to 64°C in order to measure irreversible thermal expansion. As in previous experiments in these laboratories [3], the specimen under test was placed in a quartz dilatometer in an oil bath, and subjected to 40 six-hour cycles (three hours heating and three hours cooling) over the appropriate temperature range. Axial expansion and contraction of the specimen was followed using the dilatometer, while variation of both axial and radial dimensions were determined using a micrometer. Results of these experiments are presented in Table 2.

TABLE 1

ANALYSIS OF IMPURITIES IN TNT SAMPLES

Specimen	Crystal Orientation	Impurities (%)		
		2,4-DNT	2,4,5-TNT	2,3,4-TNT
1	Random	0.42	0.12	0.12
		0.39	0.11	0.09
2	Radial	0.22	0.07	0.06
		0.18	0.06	0.06
3	"Pseudo-axial"	0.09	0.03	0.05
		0.06	0.02	0.02

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T A B L E   2

IRREVERSIBLE THERMAL EXPANSION OF TNT

Specimen	Crystal Orientation	Thermal Cycle (°C)	Irreversible Expansion		
			Axial Elongation (%)	Radial Elongation (%)	Volume (%)
1	Random	-4-47	0.50	0.40	1.30
		0-54	0.70	0.80	2.32
		10-64	1.13	1.40	3.97
2	Radial	-4-47	0.60	0.40	1.40
		0-54	0.90	0.60	2.11
		10-64	1.60	1.00	3.64
3	"Pseudo-axial"	-4-47	0.35	0.50	1.36
		0-54	0.40	1.30(0.80)	2.42
		10-64	0.87	2.00(1.40)	4.23
4	Axial	0-54	0.08	-	-
		10-64	0.10	-	-

In every case the TNT cylinder experienced a degree of irreversible thermal expansion accompanied by modification of the surface of the charge as described previously. For each crystal orientation the extent of roughening or thermal etching increased with the upper temperature of the thermal cycle. However the variation in grain size made it difficult to compare the effect in specimens of different crystal orientation. The magnitude of irreversible thermal expansion also increased with the maximum temperature experienced for each crystal orientation. This is illustrated graphically in Figure 3 in which axial elongation of the cylindrical specimens is plotted as a function of maximum temperature experienced for each crystal orientation. As was found in the previous investigation [3] these results are consistent with a critical temperature for growth of about 37°C, regardless of the crystal orientation.

The data in Figure 3 also indicate a marked dependence of growth in TNT, as monitored by axial elongation of cylindrical specimens, on the crystal orientation within the matrix. Thus material with a radial orientation (specimens 2) grew more in the axial direction than did creamed TNT with its random orientation (specimens 1), while TNT with a "pseudo-axial" arrangement of crystals (specimens 3) grew less in this direction. The single specimen with more perfect axial orientation (specimen 4) suffered almost no growth. The results in Table 2 confirm that growth of creamed TNT, with its random array of small crystals, was the same in the axial and radial directions, within experimental error. However this was not the case for the other crystal orientations. Thus radially oriented TNT (specimens 2), which experienced greater growth in the axial direction, grew less radially than did creamed TNT; conversely, cylinders in which the TNT crystals were aligned "pseudo-axially" (specimens 3) and which grew less in that direction suffered greater radial irreversible thermal expansion. Further, as the figures in parenthesis in Table 2 indicate, these specimens grew significantly less in this direction at the "collar" of random crystal orientation than they did at the ends of the specimens where the crystal alignment was more perfect as shown in Figure 2. Unfortunately specimen 4, in which the grains were more perfectly aligned throughout in the axial direction, were too brittle to allow radial measurement with a micrometer, and values for growth in this direction are unavailable.

3. DISCUSSION OF RESULTS

It has been established that irreversible thermal expansion of certain non-cubic metals depends on crystal orientation. For example, Burke and Turkalo monitored axial elongation of polycrystalline uranium rods cycled 750 times between room temperature and 550°C; selected results are presented in Table 3. A "pseudo-single crystal", in which the grains were almost perfectly aligned parallel to the axis of the rod, and which consequently generated no shearing stresses at the grain boundaries, suffered no growth. "Textured" specimens prepared by reduction by rolling at elevated temperatures, and in which the (010) crystal axes were aligned parallel to the axis of the rod (the direction of rolling) without placing further restrictions on the orientation of the grains, experienced an axial elongation of 250-550 ppm. By way of comparison a "β-heat treated" specimen consisting of an array of randomly oriented crystals grew by only 20-30 ppm. The

authors assumed that a polycrystalline specimen could be treated as an aggregate of bicrystals and that the overall distortion of the specimen would be the algebraic sum of the distortions of the individual bicrystals. "In β-treated uranium the grains are randomly oriented, the algebraic sum of distortions is zero and no growth should occur." The relatively small growth observed was ascribed to minor deviation from a truly random array of crystals. Dimensional changes in the radial direction were not reported [10].

T A B L E   3

EFFECT OF TEXTURE ON GROWTH RATE OF URANIUM ROD

(FROM BURKE AND TURKALO [10])

Cycling range: Room temperature to 550°C (1020°F) No. of cycles:750			
No.	Treatment	Texture	Growth (ppm)
1	Pseudo-single crystal	Almost perfect	0
2	β-Treated crystal	Almost random	20-30
3	5% reduction at 300°C (570°F)	Slight - (010) poles parallel rolling direction	250
4	75% reduction at 300°C (570°F)	Strong - (010) poles parallel rolling direction	550
5	75% reduction at 600°C (1110°F)	(010) + (110) poles parallel rolling direction	200

On the other hand Aitchison et al. showed that textured zirconium rods cycled 50–750°C or 400–750°C suffered only about one third of the growth of rods with randomised crystal orientation. Paradoxically, however, it was also shown that the direction of maximum growth of textured zirconium coincided with the axis of the bar from which the specimen was machined, that is the direction of the texture, suggesting that crystal orientation was the predominant variable [11].

It is apparent from results obtained in the current study that the dimensional instability of polycrystalline TNT charges on thermal cycling is also markedly dependent on crystal orientation. Thus specimens with a radial arrangement of TNT crystals (specimens 2) grew more in the axial direction and less in the radial direction than did creamed TNT (specimens 1), while samples with a "pseudo-axial" orientation of crystals (specimens 3) suffered less growth in the axial direction and more growth radially.

These observations are despite the variation of TNT grain size between the samples illustrated in Figure 2 and the variation in impurity levels present shown in Table 1. The implication is that crystal orientation is equally as important a variable in the growth of polycrystalline TNT as in the uranium and zirconium systems. Results obtained in this study also suggest that, within experimental error, three-dimensional irreversible expansion (volume) is independent of crystal orientation, notwithstanding the variation of crystal size and impurities present. Further, the growth of a pseudo-cylindrical TNT-charge such as a shell filling, prepared by the normal casting procedures which produce a radial orientation of crystals, should be predominantly axial in direction.

As discussed in a previous paper, there has been considerable confusion regarding the 2,4,6-trinitrotoluene crystal system, and both monoclinic and orthorhombic forms have been described, together with variants on each [12,13]. However the deviation from orthorhombic symmetry is slight and for most practical purposes the crystal system may adequately be described as pseudo-orthorhombic. To further complicate the picture, different authors have used different nomenclatures for the TNT unit cell [14,15,16] and assignment of coefficients of thermal expansion to the crystal axes has become confused. From the evaluation of published data on the subject [14-19] together with dilatometer records of expansion and contraction of polycrystalline TNT charges in the current study, presented in the Appendix, it was concluded that thermal expansion along the b-axis (McCrone's nomenclature [15]; the long unit cell dimension, the short macroscopic crystal dimension, and the axis of lowest refractive index, $\alpha = 1.543$) is about three times those along the other axes, which are approximately equal. However TNT crystals grown from the melt are elongated on the c-axis [8,15], and expansion in this direction takes one of the smaller values.

In the radially oriented sample 2 the individual TNT grains tend to be arranged with the c-axis aligned in a radial array about the axis of the cylinder, with the flattened {010} face parallel to that axis [8]. As a result there tends to be a "texture" of crystals with the a and b axes inclined at some angle to the axial direction of the specimen; since the coefficient of thermal expansion is greatest along the b-axis, there are frequent interactions in the axial direction between crystals of high and low expansion with little such interaction radially, the intergranular stresses generated on thermal cycling are high axially and low radially, and the growth observed parallels these intergranular stresses. On the other hand in the "pseudo-axial" sample 3 the crystals tend to be arranged with the c-axis aligned parallel to the axis of the cylinder, and an a/b texture of crystals arranged radially. There are then frequent interactions in the radial direction and few interactions along the axis of the cylinder between crystals with high and low thermal expansion in these directions. The intercrystalline stresses developed, and consequently the growth observed on thermal cycling, are therefore low axially and high radially. In the more perfect axial specimen 4 the interactions generated in the axial direction are smaller, as are the intercrystalline stresses and the growth observed. By way of comparison in creamed TNT the individual grains are randomly oriented and all axes, in particular the b-axis, are equally distributed in all orientations. As a consequence there is a proportion of crystals with the b-axes aligned in any particular direction. The intercrystalline stresses generated on thermal cycling and therefore the growth

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observed are also distributed evenly in all directions, and growth is con-
sequently not as large in any direction as may occur in a particular direc-
tion in a textured specimen. From the limited experiments carried out it
would seem that the total of growth in all directions, i.e. three-dimensional
irreversible expansion, is independent of crystal orientation (at least
provided there *is* interaction between large and small thermal expansions)
but the distribution of growth depends on crystal orientation. It is also
quite apparent that the growth of creamed TNT with its random array of
crystals is distinctly non-zero, and that growth and distortions of
individual bicrystal systems do *not* cancel each other in some algebraic
summation process. These results are consistent with the mechanism previously
postulated [3], namely that the intercrystalline stresses generated on
thermal cycling as a consequence of the anisotropic thermal expansion of TNT
are relieved by intracrystalline processes below the eutectic melting point
of TNT and its major impurities and by some intercrystalline mass transfer
process above this temperature.

4. CONCLUSIONS

Three-dimensional irreversible thermal expansion of polycrystalline
TNT appears to be invariant for the crystal orientations considered, *viz.*
random, radial and axial arrays. However, the extent of growth in a
particular direction depends markedly on the crystal orientation within the
system. Creamed TNT, with its random crystal orientation, grows equally in
all directions. Growth is larger in a particular direction if there is a
"texture" of TNT crystals with high and low coefficients of thermal
expansion, which generate large intercrystalline stresses in that direction
on thermal cycling. Growth is smaller when the TNT crystals are so arranged
that there are no such interactions and the intercrystalline stresses
generated in that direction are small. Because of the natural mode of
crystallisation of cylindrical melt-cast TNT charges, shell-fillings of TNT-
based compositions will be subject to greatest growth along the axis of the
shell. These results are consistent with the "ratchet" mechanisms previously
proposed to account for growth in polycrystalline TNT, involving the genera-
tion of intercrystalline stresses by anisotropic thermal expansion and their
relief at low temperatures by intracrystalline slip and twinning and at
higher temperatures by some mass transfer process involving the presence of
liquid eutectic at the grain boundaries.

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CORRELATION OF COEFFICIENTS OF THERMAL EXPANSION

WITH CRYSTALLOGRAPHIC AXES OF TNT

Scott considered 2,4,6-TNT to be orthorhombic; refractive indices, cell dimensions and coefficients of thermal expansion were measured, and crystallographic axes were assigned as shown in Table 4. Scott found that TNT crystals were elongated on the a or b axes depending on the solvent from which they were recrystallised, had an easy a b (001) cleavage plane and were strongly negatively birefringent. He deduced that the aromatic rings lay approximately parallel to the cleavage plane [14].

T A B L E   4

2,4,6-TNT CRYSTALLOGRAPHIC DATA
(FROM SCOTT [14])

Crystallographic Axis	Refractive Index	Unit Cell Dimension (Å)	Coefficient of Expansion
a	$\gamma = 1.717$	15	5.16×10^{-5}
b	$\beta = 1.674$	6	5.56×10^{-5}
c	$\alpha = 1.543$	40	15.36×10^{-5}

McCrone [15] also found the crystal structure to be orthorhombic, but assigned the crystallographic axes as shown in Table 5. (Note that Blomquist [16] quotes the same results, but assigns axes a, b and c parallel to α, β and γ. All other references to McCrone's work use the axes assigned in Table 5). McCrone found that the crystals were elongated on the a and c axes depending on the solvent [15]; both McCrone [15] and Williamson [8] found that TNT crystals grown from the melt were elongated on c and flattened on {010}.

Eubank and van Dolah [17] measured thermal expansion coefficients along the three crystal axes described as *short*, *intermediate* and *long*. A portion of their results are presented in Table 6. If it is assumed that these authors' identification refers to macroscopic crystal dimensions rather than unit cell dimensions, it may be concluded that the thermal expansion along the b axis (the long unit cell dimension, the short macroscopic crystal dimension, the lowest refractive index $\alpha = 1.543$) is about three times those along the a and c axes, which are approximately equal. These conclusions are consistent with the results of Scott [14] presented in Table 4.

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T A B L E   5

2,4,6-TNT CRYSTALLOGRAPHIC DATA
(FROM McCRONE [15])

Crystallographic Axis	Refractive Index	Unit Cell Dimension (Å)
a	$\gamma = 1.717$	14.85 ; 14.99
b	$\alpha = 1.543$	39.5 ; 40.0
c	$\beta = 1.674$	5.96 ; 6.10

T A B L E   6

THERMAL EXPANSION OF 2,4,6-TNT
(FROM EUBANK & VAN DOLAH [17])

TNT Specimen	Length (in)	Coefficient of Expansion (x 10^6)
Crystal 1		
Short axis	0.148	181
Inter. axis	0.584	50.5
Long axis	0.769	49.3

On the other hand it must be noted that Grabar et al.[18] concluded on the basis of birefringence studies on TNT that the "crystal axes" *short, intermediate* and *long* used by Eubank and van Dolah refer to the unit cell dimensions rather than the macroscopic crystal dimensions. Such conclusions are *not* consistent with Scott's results [14], and imply that expansion is greatest along the c axis, the axis along which TNT crystals grown from the melt are elongated [8,15]. It is interesting to note that in a companion paper by McCrone, which questions other conclusions of Grabar et al., it is stated explicitly that "the highest rate of thermal expansion lies along the b direction" [19]. Further, evidence mitigating against these conclusions may be gathered from dilatometer records of the cycling process in the

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present study. The axial expansion and contraction of the TNT cylinder
during the first thermal cycle for each experiment is shown in Table 7. (The
values quoted in arbitrary units from chart records.) Since TNT crystals
grown from the melt elongate on the c axis [8,15], crystals are aligned with
these axes oriented radially in specimens 2 and axially in specimens 3 and 4.
If the coefficient of thermal expansion was highest along this axis,
specimens 3 and 4 should both expand and contract more than specimens 1 and
2 during thermal cycling. In fact the reverse was true for all temperature
ranges. It was inferred therefore that the assignment of Grabar *et al.* was
incorrect, and expansion along the fast growing c axis was one of the lower
values.

<center>T A B L E   7</center>

<center>EXPANSION AND CONTRACTION OF TNT SPECIMENS
IN THE FIRST THERMAL CYCLE</center>

Specimen	Crystal Orientation	Thermal Cycle (°C)	Expansion*	Contraction*
1	Random	– 4–47	2.42	2.11
		0–54	2.44	2.12
		10–64	2.64	2.18
2	Radial	–4–47	2.59	2.17
		0–54	2.75	2.13
		10–64	3.41	2.18
3	"Pseudoaxial"	– 4–47	2.17	1.98
		0–54	2.05	1.85
		10–64	2.42	1.94
4	Axial	0–54	1.72	1.72
		10–64	1.70	1.69

* Expansion and contraction values are in arbitrary units extracted
from chart records.
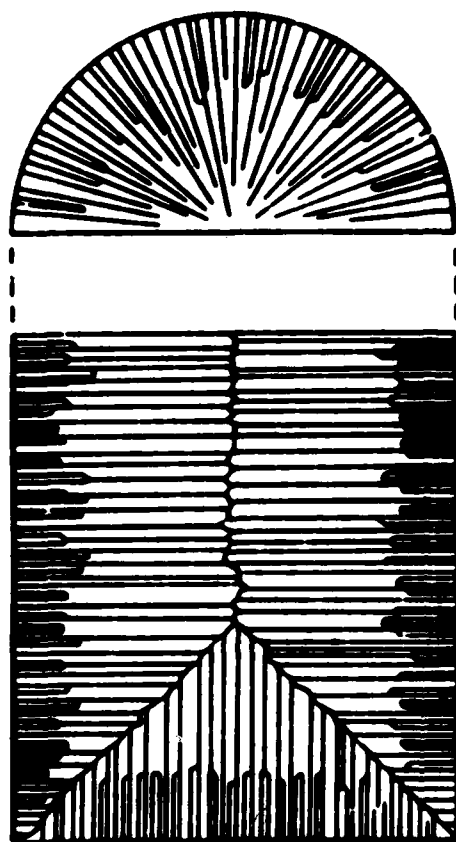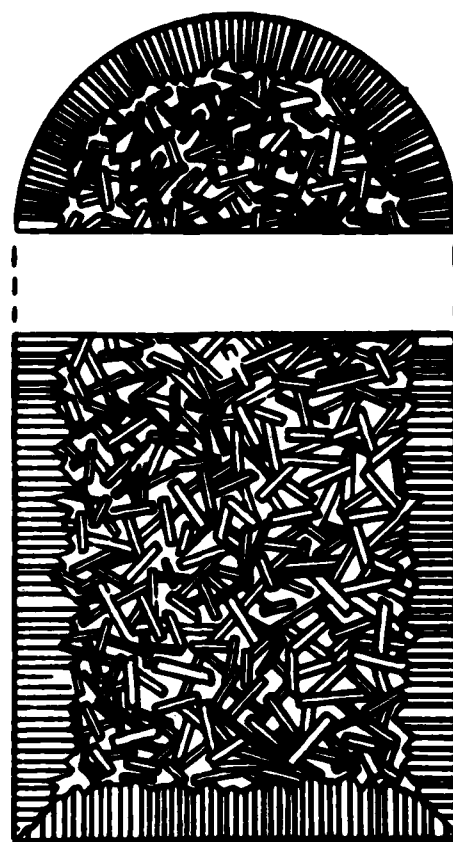
Clear-Cast TNT   TNT "Poured Cloudy"
                                        (Creamed TNT)

FIG. 1 - Crystal Structure of Clear-Cast TNT and TNT
         "Poured Cloudy" (Creamed TNT).

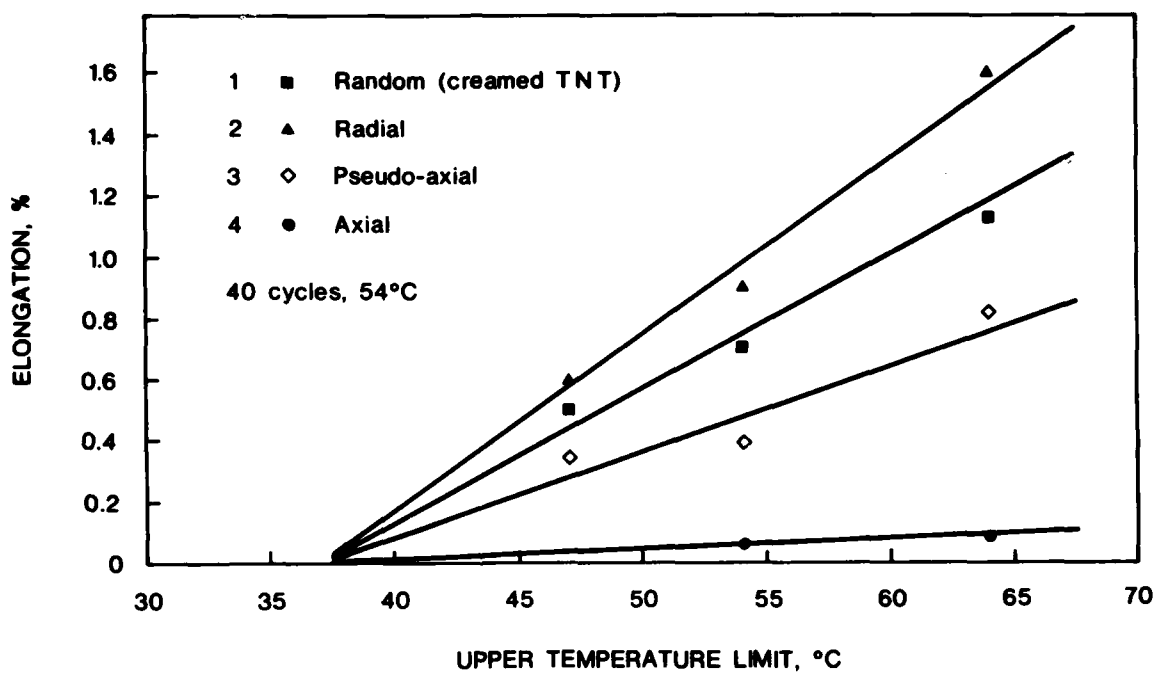| (1) | (2) | (3) | (4) |
| Random | Radial | "Pseudoaxial" | Axial |

FIG. 2 - Crystalline Structure of Cast TNT Cylinders.

FIG. 3 - Axial Elongation (Growth) of TNT Cylinders with Various
Crystal Orientations.

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